WATER TRANSPORT ACROSS CATION-EXCHANGE MEMBRANE.
I. EXPERIMENTAL TECHNIQUE. INFLUENCE OF THE CONCENTRATION AND TEMPERATURE ON THE WATER TRANSPORT NUMBER
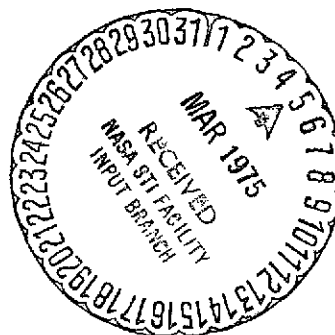
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16. Abstract We developed an automatic technique for measuring electroosmotic flows and applied it to measurement of water transport numbers of two cation-exchange membranes under the influence of various parameters. The results show a strong dependence between water transport number and concentration in the range 0.01 to 1 N. The nature of the ion is important, while the influence of the temperature is small (about 0.1% per degree at 25-80°C). Finally, we compared the measured water transport numbers with those calculated according to Manning's model in the case of sodium chloride at different concentrations and found that the model gives a satisfactory agreement between the experimental and calculated values.

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Symbols

a_y	Distance between two charged groups in the inflated membrane
$a_y{}^\circ$	Distance between two charged groups in the dry membrane
$\overline{C}_i$	Molar concentration of i in the membrane
$\overline{C}_s$	Molar concentration of salt in the membrane
e	Elementary charge
E^*	Electric field in the CGS system
E	Electric field in the SI system
F	Faraday
I	Current density in $A \cdot cm^{-2}$
$(J_i)_c$	Flow of i in relation to the cell, expressed in $moles \cdot cm^{-2} \cdot s^{-1}$
$(J_i)_b$	Flow in i in relation to the barycenter, expressed in $moles \cdot cm^{-2} \cdot s^{-1}$
$(J_v)_c$	Voluminal flow in relation to the cell
K	Debye-Hückel screen parameter
k	Boltzmann's constant
M_i	Molar mass of i in grams
m_g	Mass of inflated membrane in grams
m_s	Mass of dry membrane in grams
m_o	Mass of inflating water in grams
N	Avogadro's number
T	Temperature
t_i	Transport number of i defined by equation (5)
t_o	Water transport number
$t_{o(app)}$	Apparent water transport number
T_g	Inflation rate

U_b	Barycentric speed, $cm \cdot s^{-1}$
$\overline{V}_i$	Partial molar volume of i
V_D	Tape speed of recording machine
V_E	d.d.p. at the limits of the potentiometer
V_S	Caliber of recording machine
$\overline{V}_S$	Partial molar volume of salt in cm^3
$\overline{V}_O$	Partial molar volume of water in cm^3
$\overline{V}_2$	Partial molar volume of the co-ion in cm^3
W	Algebraic value of the membrane charge
X	Membrane capacity
α	Parameter defined by equation (11)
ϵ	Dielectric constant
λ	Parameter defined by equation (10)
ρ_O	Voluminal mass of the inflating solution
ρ_S	Voluminal mass of the dry membrane
ΔL	Change of position read on the recording machine
Δt	Time needed for a volume variation ΔV
ΔV	Volume variation of the receiving compartment
$\Delta \lambda$	Length of the recording
η	Dynamic viscosity
τ	Interior diameter of the capillary
χ	Conductivity of the membrane in $\Omega^{-1} \cdot cm^{-1}$
$0,1,2,S$	Water, counter-ion, co-ion, salt

WATER TRANSPORT ACROSS CATION-EXCHANGE MEMBRANE.
I. EXPERIMENTAL TECHNIQUE. INFLUENCE OF THE CONCENTRATION AND TEMPERATURE ON THE WATER TRANSPORT NUMBER

M. Demarty[1], A. Maurel[2] and E. Selegny[3]

Introduction

Since the discovery of ion-exchange membranes and their application to industrial processes, the study of electrokinetic phenomena, among them electroosmosis, has been the object of several study projects. Electroosmosis has an influence, at times considerable, on the optimal conditions of the unfolding of technological processes.

The electroosmotic flow results from the presence of non-mobile charged groups (fixed charges) in the interior of the ion-exchange membrane. In fact, as we apply an electric field across an exchange material separating a solution of electrolyte, the ionized exchange groups are retained by covalent bonds and cannot change positions; the result is then a movement of the solvent (in the opposite direction from the charges), which thus guarantees a change of position in relation to the barycenter of the system. The water transported by electroconvection is generally decomposed into two parts: water tightly bound into the compensating ions by electrostatic forces traveling at the same speed, and water drained by viscous force during the passage of the ions across the membrane.

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* Numbers in the margin indicate pagination in the foreign text.

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In this study we present, on the one hand, an automatic method for the measurement of very small electroosmotic flows without modifying the concentrations of the solutions very much. On the other hand, we will compare the results obtained with the water transport numbers calculated according to Manning's theory.

I. Review of Methods for the Measurement of Electroosmotic Flows

The measurement of water transport in electrodialysis may be obtained with different methods:

1) measuring the variations of mass and concentration of the donor and acceptor compartments [1, 2, 3]. The great inconvenience of this method lies in the difficulty of previous removal of all of the solution from the compartments. On the other hand, the possible deformations of the membrane do not cause disturbances as is the case in the "voluminal" method;

b) measuring the volume variations of the solutions flooding the membrane. A great number of researcher have adopted this method, bringing different variants into it [4, 17].

The measurement cell is made up of two compartments separated by a membrane and surmounted by calibrated capillaries.

Other methods make it possible to observe the volume variations. Sosipatrov et al. [5] measured the capacity of a condenser whose dielectric is made up of isoamylic alcohol and air. The measurement cell is connected to the condenser by a U-shaped tube, and the volume variations produce a modification of the capacity. This method requires a specially constructed set of instruments and the use of a dielectric insoluble in the medium studied, whose volatility is small and dielectric constant high.

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Teorell, Bary and Hope have presented a brief description [5, 7] of a method for measuring volume variations by using a photoelectric system. A U-shaped tube connecting the two compartments is partly filled with a dense liquid immiscible with water and colored. The luminous intensity received by the photoelectric cell is a function of the level of the colored liquid. With the help of a calibrated curve, they are able to determine the volume variations in the cell during work.

By using a photoresistance, we developed a technqiue which makes it possible to observe and record the electroosmotic flow in a measurement cell or, eventually, in an electrodialyzer.

II. Automatic Measurement Method

The equipment used for these measurements is presented in Fig. 1; it is made up of several separate parts:
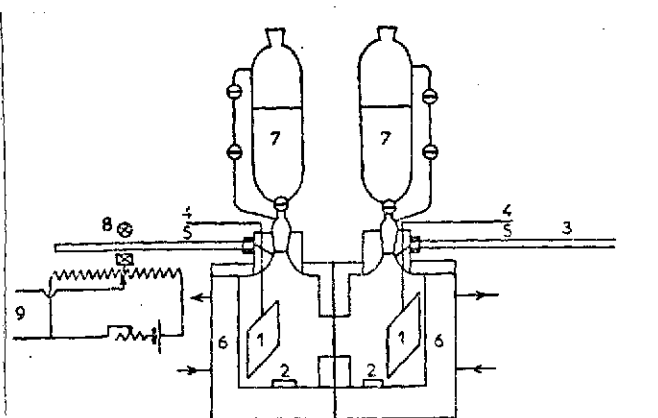

Fig. 1. Equipment for measuring electro-osmotic flow: 1. electrodes in Ag/AgCl; 2. magnetic bars; 3. capillaries; 4. reverser; 5. stabilized feeding, Tacussel CGR; 5. thermostatic jacket; 7. filling ampullas; 8. photoelectric system which makes it possible to observe the change of position of the meniscus; 9. exit toward recording machine or system of acquisition and treatment of data.

a) Measurement Cell

It is made up of two identical half-cells separated by the membrane under study. A set of masks placed on both sides of the membrane makes it possible to modify its useful surface at will, while watertightness is guaranteed by two flat rubber joints. With this setup, it is unnecessary to use grating to support the membrane, whose surface is small.

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The two cells are closed by two plugs on which the capillaries, the working electrodes, and the filling ampullas are fixed.

The plugs have a conical base, which allows the bubbles to rise completely at the time of filling and the gases dissolved in the solution studied to depart during measurements at high temperatures.

The electrodes are made up of silver plates covered with silver chloride through electrolysis according to the usual techniques [8].

The filling ampullas are fixed onto the plugs by conical ferrules, which are lubricated in order to avoid all leakage. A small rubber tube placed between the two lateral stopcocks makes /813 it possible to change the position of the meniscus in the capillaries by squeezing with a Mohr's pinchcock.

The capillaries are fixed horizontally onto the cells by means of conical ground joints. Their diameter may vary according to the test, but in our case it is about 2.5 to 0.01 mm.

Agitation of the solutions is guaranteed by magnetic bars which turn at a speed of over 6000rpm. Under these conditions, the solution may be considered to be homogeneous from the standpoint of concentration and temperature.

The cell is surrounded by an exterior jacket containing a thermostatic liquid whose temperature is adjusted to 5/100th of a degree.

b) Feed Circuit

The current supplied to the cell is produced by a regulated intensity source operating in the range 0.8-250 mA.

The electrodes are alternately anodes and cathodes. Commutation is guaranteed by a timer which allows a reverser to swing for predetermined periods of time, varying from 1 to 12 min. The purpose of this operation is to operate in the immediate neighborhood of the initial concentration of the filling solutions.

c) Detection Circuit

The position of the meniscus in the measurement capillary is marked by a photoelectric cell illuminated by a small lamp. When the position of the meniscus changes, the optical beam swerves, and the photoelectric cell moves laterally in order to find maximal illumination (Sefram SN125 level follower).

However, this detection system is difficult to use with very fine capillaries; in order to improve it, we must use much more perceptible photodiodes. The photoelectric cell is mechanically connected to the slider of of a potentiometer. A cell-rheostat system makes it possible to maintain a permanent level of 1 V (V_E) at the extreme terminals of the winding.

d) Amplification and Recording Circuit

The voltage gathered at the terminals of the potentiometer is sent to the recording machine operating in one of the ranges (V_S) of 10, 25, or 50 mV, according to the case, which makes it possible to fictively multiply the change of position of the meniscus by 100, 40, and 20.

The speed with which the paper changes (V_D) is selected so that we can obtain straight lines, whose gradients are easily measured.

III. Calculation of the Water Transport Number

The water transport number t_o is defined as the number of moles of water transported by one Faraday of current across 1 cm^2 of membrane. We defined a measured water transport number by:

$$t_{oM} = \frac{\Delta V.F}{\overline{V}_o.1.\Delta t}$$

(1)

The explanation of the symbols is given in an annex.

It is easy to express the water transport number as a function of the characteristics of the system used; we obtain:

$$t_{oM} = K \frac{1}{I tg\theta}$$

(2)

with

$$K = \frac{\tau^2.\pi.V_S.V_D.F}{\overline{V}_o.4.V_E.}$$

The only measurement to be accomplished, then, is the determination of the angle θ of the curves with the horizontal line; we may also accomplish the measurement of the gradient automatically by using a tachometer or by injecting the voltage gathered at the terminals of the potentiometer into a system of data acquisition and processing. In this case, the calculation of the water transport number is obtained directly.

The real water transport number is obtained by the relation [9]:

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$$t_0 = t_{oM} - t_1 \frac{\overline{V}_s}{\overline{V}_0} + \left(\frac{\overline{V}_{AgCl} - \overline{V}_{Ag}}{\overline{V}_0} \right)$$

(3)

The second term in the expression represents the contribution of salt to the measured voluminal flow and the volume variations of the electrodes.

As equation (2) shows, measurements of t_{oM} will be more precise the closer the angle θ is to 45°. The estimated maximal theoretical error is in the range of 6%, but, in fact, the reproducibility of the tests is over 3%.

IV. Experimental Results

Numerous researchers have studied the different factors which modify electroosmotic flow. However, the influence of temperature has attracted the attention of only a few. The principal conclusions have been gathered together by Lakshminaraianaiah [4].

The two membranes used here have fairly dissimilar characteristics; the first (I) is of commercial origin (Ionac 3470 XL), while the second (E) was obtained by chlorosulfonation and subsequent hydrolysis of a polyethylene film [10]. The different samples used first underwent cycles of concentration variation and heat treatment (between 20 and 80°C), which guarantees better reproducibility of the measurements at different temperatures [11, 12]. We applied our method to the determination of water transport numbers of these membranes in the presence of alkaline chlorides.

The results presented in Tables I to IX and Figs. 3 and 4 are averages obtained for tests repeated 20 or so times with different samples and different current densities.

TABLE I. WATER TRANSPORT NUMBER OF THE MEMBRANE E IN THE PRESENCE OF LITHIUM CHLORIDE AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

$t \rightarrow$ $C \downarrow$	25 °C	35 °C	45 °C	55 °C	65 °C	80 °C
1 N	14.4	14.6_2	14.9_5	15.2	14.6_9	15.3_8
0,3 N	22.6	22.5_4	22.7_4	23.0_4	23.1_6	23.2
0,1 N	28.3_3	29.3_4	30.3_2	31.6_0	32.8	33.2
0,03 N	30.7_1	31.0_5	31.7_1	32.5_5	32.6_9	32.7_6
0,01 N	31.3_2	32.2_1	32.0_3	31.3_3	32.6_9	33.0_1

TABLE II. WATER TRANSPORT NUMBER OF THE MEMBRANE E IN THE PRESENCE OF SODIUM CHLORIDE AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

$t \rightarrow$ $C \downarrow$	25 °C	35 °C	45 °C	55 °C	65 °C	80 °C
1 N	$8,4$	$8,5$	8.6_8	8.72	9	8.65
0,3 N	15.0_3	15.5_2	15.3	15.2_8	15.1	15.3_6
0,1 N	$18,3$	18.7_1	$18,8$	17.7_8	18.5	19.0_9
0,03 N	21.4_6	21.3_3	20.9_6	21.0	21.8	22.1
0,01 N	22.4	22.4_5	22.9_3	22.8	22.9_6	23.0_3

TABLE III. WATER TRANSPORT NUMBER OF THE MEMBRANE E IN THE PRESENCE OF POTASSIUM CHLORIDE AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

$t \rightarrow$ $C \downarrow$	25 °C	35 °C	45 °C	55 °C	65 °C	80 °C
1 N	5.0_1	5.1	5.2_7	5.3	5.1	5.3_6
0,3 N	9.4_8	9.6	9.7_5	9.8_2	9.9_1	10.0_2
0,1 N	12.2_1	12.2_8	12.2_4	12.3_1	12.4_1	12.6
0,03 N	13.8_2	13.8_4	13.9_2	14.0_8	14.1_4	14.2_6
0,01 N	14.8_2	14.9_0	15.1_2	15.0_6	15.2_8	15.3_3

TABLE IV. WATER TRANSPORT NUMBER OF THE MEMBRANE E IN THE PRESENCE OF RUBIDIUM CHLORIDE AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

C $\quad t \rightarrow$	25 °C	35 °C	45 °C	55 °C	65 °C	80 °C
1 N	$6{,}9_4$	$7{,}1_2$	$7{,}3_3$	$7{,}3_3$	$7{,}4_6$	$7{,}4$
0,3 N	$9{,}4_8$	$9{,}6$	$9{,}6_8$	$9{,}7_7$	$9{,}9_2$	$9{,}9_4$
0,1 N	$11{,}1$	$11{,}2$	$11{,}3_1$	$11{,}4$	$11{,}5_8$	$11{,}6_2$
0,03 N	$12{,}4_2$	$12{,}3_6$	$12{,}5_3$	$12{,}6_8$	$12{,}6_2$	$12{,}9_0$
0,01 N	$13{,}1_2$	$13{,}1_9$	$13{,}3_8$	$13{,}6_4$	$13{,}7$	$13{,}7_8$

TABLE V. WATER TRANSPORT NUMBER OF THE MEMBRANE E IN THE PRESENCE OF CESIUM CHLORIDE AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

C $\quad t \rightarrow$	25 °C	35 °C	45 °C	55 °C	65 °C	80 °C
1 N	$7{,}7_2$	$7{,}7_7$	$7{,}8_1$	$7{,}8_3$	$7{,}9_2$	$7{,}9_9$
0,3 N	$10{,}7_8$	$10{,}8_2$	$10{,}9_4$	$10{,}9_1$	$11{,}0_1$	$11{,}1_2$
0,1 N	$12{,}1_6$	$12{,}2_8$	$12{,}3_4$	$12{,}3_3$	$12{,}4_1$	$12{,}4_3$
0,03 N	$12{,}5_7$	$12{,}5_0$	$12{,}6_4$	$12{,}7_2$	$12{,}8_2$	$12{,}9_4$
0,01 N	$13{,}2_1$	$13{,}1_3$	$13{,}3_8$	$13{,}4_8$	$13{,}6_1$	$14{,}1$

TABLE VI. WATER TRANSPORT NUMBER OF THE MEMBRANE I IN THE PRESENCE OF LITHIUM CHLORIDE AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

C $\quad t \rightarrow$	25 °C	35 °C	45 °C	55 °C	65 °C
1 N	$10{,}8_6$	$10{,}8_8$	$11{,}0_6$	$11{,}1$	$10{,}8_3$
0,3 N	$12{,}2_4$	$12{,}3_1$	$12{,}3_9$	$12{,}3_2$	$12{,}7_4$
0,1 N	$13{,}0_6$	$12{,}8_1$	$13{,}2_1$	$13{,}7_1$	$13{,}8$
0,03 N	$13{,}4_8$	$13{,}9$	$14{,}2_1$	$14{,}6_5$	$14{,}8_3$
0,01 N	$13{,}4_2$	$13{,}5_2$	$14{,}1_4$	$14{,}5_2$	$14{,}6_7$

TABLE VII. WATER TRANSPORT NUMBER OF THE MEMBRANE I IN THE PRESENCE OF SODIUM CHLORIDE AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

C / $t \rightarrow$	25 °C	35 °C	45 °C	55 °C	65 °C
1 N	8.1_2	8.0_6	8.0_9	8.2_7	8.3
0.3 N	8.1_4	8.2_8	8.2_4	8.4_4	8.5_2
0.1 N	8.2_4	8.3	8.2_3	8.4_3	8.9
0.03 N	8.1_7	8.0_7	8.3_8	8.5_3	8.7_5
0.01 N	8.4	8.6_4	8.7_2	8.7_8	8.7_2

TABLE VIII. WATER TRANSPORT NUMBER OF THE MEMBRANE I IN THE PRESENCE OF POTASSIUM CHLORIDE AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

C / $t \rightarrow$	25 °C	35 °C	45 °C	55 °C	65 °C
1 N	6.7_5	6.9	6.9_7	7.2_5	7.4_6
0.3 N	6.7_7	6.8	7.1_4	7.2_2	7.6
0.1 N	6.5_8	6.8_9	7.0_1	7.1_3	7.1_9
0.03 N	6.6_5	6.6_5	7.0	7.3	7.7_9
0.01 N	6.8	6.8_2	7.0	7.2_8	7.4_6

TABLE IX. WATER TRANSPORT NUMBER OF THE MEMBRANE I IN THE PRESENCE OF HYDROCHLORIC ACID AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

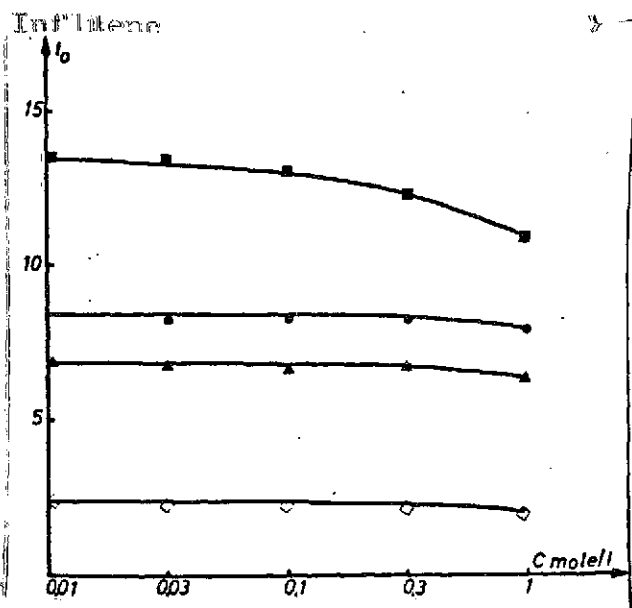| C / $t \rightarrow$	25 °C	35 °C	45 °C	55 °C	65 °C
1 N	2.1	2.2	2.3_8	2.4_7	2.5_4
0.3 N	2.1_6	2.1_4	2.3	2.5	2.5_8
0.1 N	2.2_7	2.3	2.3_2	2.5_7	2.6_1
0.03 N	2.1_2	2.2_8	2.4	2.4_8	2.6_3
0.01 N	2.2	2.3_4	2.4_6	2.6_3	2.7

Fig. 2. Variation of the water transport number as a function of the concentration of the solutions with the membrane I at 25°C. ■ LiCl; ● NaCl; ▲ KCl; ◇ HCl.
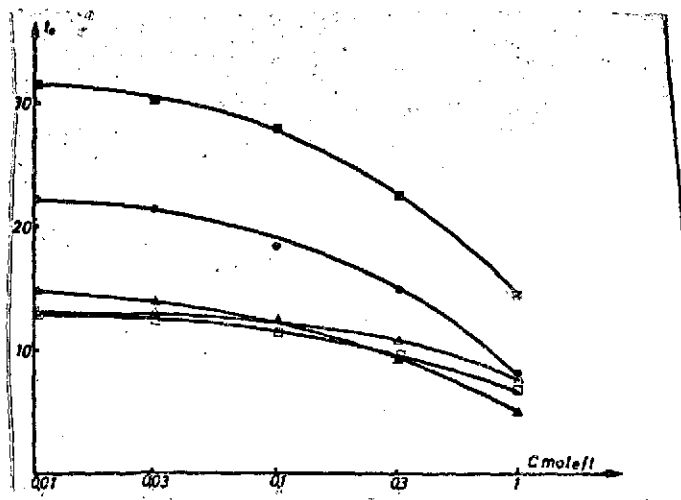

Fig. 3. Variation of the water transport number of the membrane E at 25°C as a function of the solutions. ■ LiCl; ● NaCl; ▲ KCl; □ RbCl, o CsCl.

Influence of Current Density

We confirmed that the current density did not have any effect on the water transport numbers in the area studied (5 to 50 mA/cm^2) for solutions 0.3 N and 1 N, and 5 to 20 mA/cm^2) for others) when sufficient agitation is imposed.

In the case of tests con- /815 ducted under natural convection (absence of all agitation) we noted an appreciable dependence of t_o on I. The water transport number increases quite clearly when the current density decreases; when the values of I are high, there is a tendency toward a level which is inferior to t_o obtained in the presence of agitation. We attribute these effects to the modification of the polarization layers during the test [14, 15].

Influence of the Nature of the Ion

As we can see in Figs. 2 and 3, the water transport numbers of the membrane (I) diminish
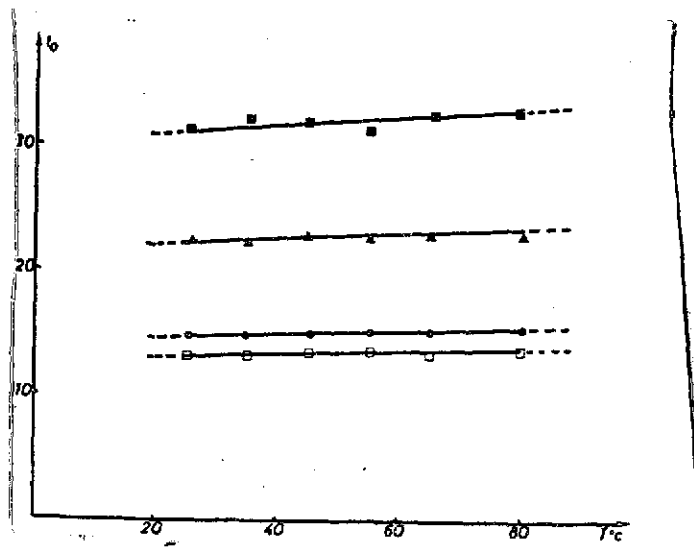
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Fig. 4. Variations of the water transport number of the membrane E as a function of the temperature of the solutions in the case of 0.01 N solutions.
■ LiCl; ▲ NaCl; ● KCl; □ RbCl.

in the order Li > Na > K > > H. With the membrane (E), the order of the variation is Li > Na > Cs ≃ Rb > K, at least with concentrations below 0.1 N; beyond that, the order undergoes modifications.

We also observe that the last three ions have a similar behavior, and that there is very little difference in the water transport numbers. We can further notice that the water transport number of the Cs^+ ion is always greater than that of the Rb^+ ion. This effect has already been noticed [4] in various, very different cationic membranes. Nevertheless, the researchers give results for weak concentrations only, generally 0.01 N.

A qualitative explanation of the influence of the ions of the alkaline series on the water transport numbers can be given by examining their behavior toward strong polyelectrolytes.

The larger the hydrated ion is (the case of lithium), the greater is its approach distance to the fixed charges of the polyion; this ion has little facility to compensate for the charges carried by the matrix. The effective charge of the polyion, then, is high. In the case of a soluble polyelectrolyte, the result is a high pK and high viscosity and a considerable inflation for the resins in the ion-exchange membranes. These effects diminish as we pass from lithium to cesium.

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In an ion-exchange membrane the inflating solution carries a charge opposite to that of the matrix in order to respect the electroneutrality of the system. As a first approximation we may concede that the higher this charge is, the more important the electroconvection will be; this would justify the observation of a /816 water transport number which decreases from lithium to cesium.

However, we must emphasize the fact that the parameter influencing the electroconvection is not the charge but the voluminal density of the charge of the solution,aas the Naviers-Stokes equation shows; but,asince we know that the membrane inflates more in the case of lithium than in the case of cesium, it is difficult to conjecture in which direction the voluminal density of the charge varies.

Let us finally remember that part of the water is transported in the form of hydration water for the ions; consequently, we may concede that this contribution is more important for the alkalis at the top of the column.

Influence of Temperature

As we can seen in Tables I to IX and in Fig. 4, ihethe range of 25-80°C, an increase in temperature increases the water transport number, no matter what the compensating ion is. On the other hand, George and Courant [13] find a slight decrease between 10 and 40°C when using the Nepton CR 61 membrane.

In our case, we must observe, above all, thattthe variations are small (in the range of 0.1% per degree) when the decreasemin the viscosity of the medium, as well as the dehydration of the ions [19],ccould lead us to anticipate more considerable modifications. The conductivity of the membranes is also strongly influenced by the temperature (in the range of 2% per degree).

The variations of the different parameters should therefore compensate for each other.

Influence of the Concentration of the Solution

In Figs. 2 and 3 we traced the water transport number as a function of the logarithm of the concentration of the electrolyte solution.

For the membrane (E), the water transport number diminishes in all cases when the concentration increases. The effect is the more obvious the more of the solvent the compensating ion "drains." For example, for Na^+, t_o passes from 22.3 to 8.4 in the region of 0.01 to 1 N, that is, to one-third.

On the other hand, in the case of the Ionac membrane, the water transport numbers for the Na^+ and K^+ ions are much smaller, and the influence of the concentration is practically included in the experimental error.

The decrease in the water transport number which takes place when the concentration of the solutions is increased may be attributed to the penetration of salt into the membrane. In fact, this penetration increases the screen effects between the fixed charges of the matrix; the result is a decrease in the electrostatic repulsions between the exchange sites, which does not explain a decrease in inflation. Besides, the transport number of the counter-ion is lowered. These effects cooperate in decreasing the transport of water.

V. Calculation of the Water Transport Number Across an Ion-Exchange Membrane

The apparent water transport number, defined as the quantity of solution transported by one Faraday of current, can be ex-

expressed by the following relation in the case of an electrolyte 1-1 [9]:

$$t_{0(app)} = \frac{M_2}{M_0} - \frac{\overline{V}_2}{\overline{V}_0} + t_1\left(\frac{\overline{V}_1}{\overline{V}_0} - \frac{M_1}{M_0}\right) + \frac{U_b F \overline{V}_0}{\overline{V}_0 I M_0}\Sigma \overline{C}_i M_i \tag{4}$$

The quantity $\dfrac{\overline{V}_0}{M_0}\Sigma \overline{C}_i M_i$ represents the voluminal mass of the solution in the membrane; as a first approximation we take it to be equal to 1. U_b is the barycentric speed, $\overline{V}_1$ represents the partial molar volume of the different species, M_i is the molar mass of i, and i = 0, 1, 2 for the water, the counter-ion and the co-ion, respectively.

The transport number t_i is defined by:

$$t_1 = \frac{F(J_1)_c}{I} \tag{5}$$

where $(J_1)_c$ is the flow of the cation marked in relation to the cell.

The water transport number is connected with the apparent transport number by:

$$t_{0(app)} = t_0 + t_1\frac{\overline{V}_1}{\overline{V}_0} - \frac{\overline{V}_2}{\overline{V}_0} \tag{6}$$

By identifying (6) and (4) we obtain:

$$t_0 = \frac{M_2}{M_0} - t_1\frac{M_1}{M_0} + \frac{U_b F}{\overline{V}_0 I} \tag{7}$$

In order to express U_b, it is necessary to resolve the Naviers-Stokes equation

$$\nabla^2 U_b = \nabla P - F$$

Several researchres have done this either by using a capillary model [20, 21, 22] or by using a network of discrete charges [23].

We will use Manning's results, which seem satisfactory in the case of membranes whose charge density is high and inflation considerable.

-- In this model the membrane is assimilated into a network of discrete charges whose mesh constants are (a_x, a_y, a_z); the solution penetrates the membrane completely, but there is no restriction as to its concentration. The electric field is applied in the direction of x.

In order to resolve the Naviers-Stokes equation, the author expresses the pressure gradient and the voluminal force in the form of a Fourier series, and uses the Poisson-Boltzmann linearized equation.

Under these conditions, the barycentric speed is expressed by the following relation

$$\eta U_b = -eE^* NXWK^{-2}\{\pi\alpha \coth(\pi\alpha) - 1\}$$

in which K is the Debye-Hückel screen parameter. It is directly /817 connected with the minimum approach distance of the charges

$$K^2 = \lambda N \Sigma_i \overline{C}_i z_i^2 = \lambda N(X + 2\overline{C}_s) \qquad (9)$$

$$\lambda = \frac{4\pi e^2}{\varepsilon kT} \qquad (10)$$

16

X is the capacity and $\overline{C}_S$ is the concentration of the salt in the membrane.

The parameter α is defined by:

$$\alpha = a_y K/2\pi$$

(11)

where a_y is the distance between two charges.

We can now express the water transport number by introducing equations (8), (9), (10), and (11) into equation (7) and by observing that the electric field is connected with the current density by the expression:

$$I = \chi E$$

(12)

in which χ is the conductivity of the membrane expressed in $\Omega^{-1} \cdot cm^{-1}$.

$$
\begin{aligned}
t_0 &= \frac{M_3}{M_0} - t_1 \frac{M_f}{M_0} \\
&+ \frac{K_1 X}{(X+2\overline{C}_s)\chi} [a_y L(X+2\overline{C}_s)^{1/2} \coth(a_y L(X+2\overline{C}_s)^{1/2}) - 1] \\
K_1 &= \frac{F}{\lambda \eta \overline{V}_0 300} = 1{,}075 \\
L &= \left(\frac{\pi e^2 N}{\varepsilon kT}\right)^{1/2} = 3.67 \cdot 10^6
\end{aligned}
$$

(13)

In the calculation of K_1, we have assumed the viscosity of the medium to be very little different from that of water, or $0.80 \cdot 10^{-2}$ poises at 25°C.

In expression (13), the molar masses are expressed in grams and the concentrations in moles per cm^3.

All parameter of the equation are measurable except the parameter "a_y," which is the distance between the different

charges of the network. This parameter will vary with the infla-
tion of the membrane, and cannot be obtained experimentally. We
also tried to connect it with an "intrinsic" parameter $a_y{}^o$, which
corresponds with the dry membrane.

In order to do this, we will take an extremely simple model,
and assume that the ionizable sites of the membrane are placed
on the vertices of a cube whose edge is a_y:

The volume of this cube can be connected to the voluminal
mass of the matrix by

$$(a_y)^3 = \frac{m_t}{\rho_t}$$

(14)

When the exchanger is is contact with a solution, we in-
crease the volume of the elementary cube:

$$(a_y)^3 = \frac{m_t}{\rho_t} + \frac{m_0}{\rho_0}$$

(15)

where m_0 is the mass of the solution which penetrates inside the
membrane and ρ_0 is its voluminal mass.

In order to write equation (15), we assume the additivity of
the volumes, that is, that there is very little interaction between
the solvent and the matrix and that the voluminal mass of the
solution differs very little from that of water.

On the other hand, we define the inflation rate of the mem-
brane by:

$$T_g = \frac{m_g - m_t}{m_g}$$

(16)

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By combining (14), (15), and (16), we obtain a relation between a_y and $a_y{}^O$, in which $a_y{}^O$ is an intrinsic value of the polymer.

$$(a_y)^3 = (a_y^o)^3 \cdot F(T) \tag{17}$$

with

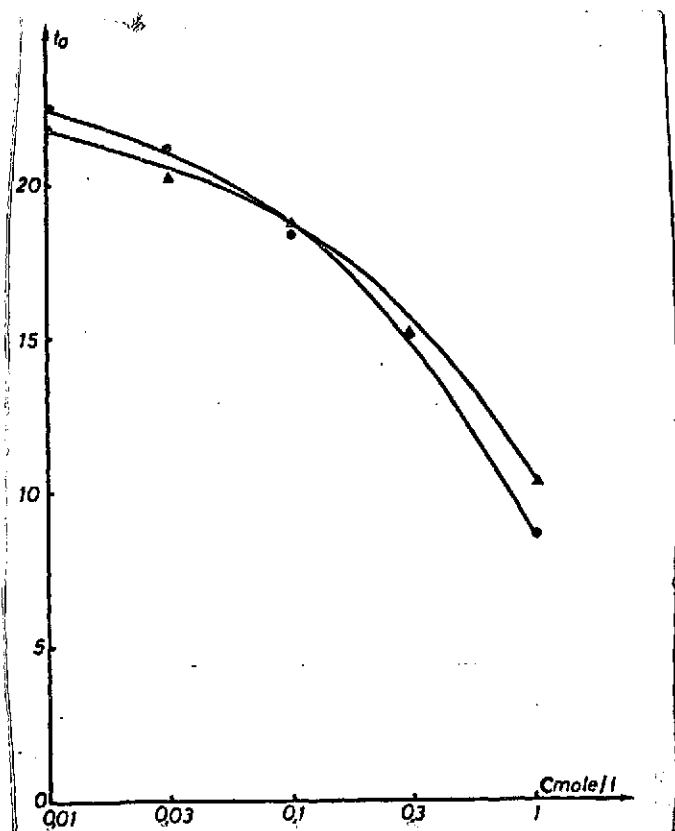$$F(T) = 1 + \frac{\rho_i}{\rho_0} \frac{T_g}{1 - T_g}$$

Fig. 5. Variation of the water transport number as a function of the concentration of the solutions. Membrane E with NaCl. ● Measured values; ▲ calculated values.

Comparison Between the Experimental and Calculated Results

We calculated the water transport number for the membrane (E) in the presence of NaCl at different concentrations by using equation (13). The results are reported in Table X and Fig. 5. We adjusted the parameter $a_y{}^O$ in such a way that there was agreement between the experimental values and the calculated ones for a 0.1 M concentration.

We are led to assume a value $a_y{}^O = 4.6$ Å, which is much smaller than the result (16 Å) obtained by Manning [23] with a membrane whose inflation was comparable to ours. The

TABLE X. WATER TRANSPORT NUMBER CALCULATED FOR THE MEMBRANE E IN THE PRESENCE OF NaCl AT DIFFERENT CONCENTRATIONS AT 25°C.

$$a_y^o = 4.67 \text{ Å}, \quad \rho_s = 1.8$$

C eq.L⁻¹	X 10⁴ eq.cm⁻³	χ 10² Ω.cm⁻¹	C̄ₛ 10⁶ eq.cm⁻³	T_y	a_y Å	t_o Measured	t_o Calculated
0,01	9	0,965	3,9	C.718	7,32	22,4	21,8
0,03	9,1	0,975	6,2	0,387	7,06	21,5	20,2
0,1	9,2	0,990	16,5	0,651	6,8	18,3	18,8
0,3	9,4	1,06	88,3	0,579	6,35	15,03	15,1
1	9,7	1,33	282,4	0,481	5,89	8,4	10,4

reresults show that this model makes it possible to give a satis-factory explanation of the variation of the water transport number as a function of the concentration in the area studied.

Conclusions

We developed an automatic method for measuring electro-osmotic flows, which is derived from the capillary technique. The use of a photoelectric system makes it possible to observe the change of position of the meniscus in the capillary and to provide an electric voltage proportional to it. The possibility of amplifying the movements of the fluids about 100-fold makes it possible to measure extremely small flows.

The method was applied to the measurement of the water transport numbers of two cation-exchange membranes, while varying the concentration of the solutions, the nature of the electrolytes, and the temperature.

The results show that the current density does not have any influence on the electroosmotic flows if the agitation of the solutions flooding the surface is sufficient. In the absence of

agitation, we observe an increase in the water transport number at low current densities.

Studies concerning this effect are the subject of separate publications [14, 15].

The measurements of the water transport in the concentration range of 0.01 N to 1 N show a strong dependence between t_O and the concentration. The effect is the weaker the smaller the t_O of the ion is. This explains to us why we do not obtain a variation for Na^+, K^+, and H^+ with the Iönac membrane.

The increase in the concentration causes a considerable penetration of salt inside the membrane. This penetration of salt diminishes the effective charge of the membrane (screen effect), that is, the convection. Further, the membrane deflates, and so decreases the hydraulic permeability.

The temperature has only a slight influence on t_O, and we observe a slight increase, in the range of 0.1% per degree, in the area studied (25 to 80°C).

The nature of the compensating ion is of great importance for electroosmotic flows. t_O decreases in the order Li, Na, K, Cs, Rb at low concentrations. In all cases, the Cs^+ ion gives the membrane a greater water transport number than Rb^+.

A qualitative explanation of the influence of the nature of the ions can be found by studying their behavior toward strong polyelectrolytes.

On the other hand, we tried to calculate the water transport numbers by using Manning's model of discrete charges [23]. The results show that the equation makes it possible to represent the variations of the experimental curves, but the agreement is only semi-quantitative.

But this model cannot explain the effects due to polarization that we observed while measuring the water transport number as a function of the current density under natural convection.

An experimental and theoretical study of the influence of polarization has been developed and is the subject of the following publications [14, 15].

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